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(54) **Ink-jet recording sheets**

(57) An ink-jet recording sheet comprises a layer of water-soluble polymer coating on a support having a water absorptivity of not more than 30 g/m², when measured in accordance with JIS P8140.

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SPECIFICATION

Ink-jet recording sheets

This invention relates to an ink-jet recording sheet, and more particularly, to an ink-jet recording sheet comprising a support of low water absorptivity which has disposed thereon a layer of water-soluble polymer as an ink-jet recording layer. The resulting recording sheet can be used to provide a multicolor image of high density, resolution and good color reproduction.

Because of its quietness, fast recording capability and adaptability to paper of ordinary grade, ink-jet recording is becoming increasingly popular, having as one of its applications a terminal printer. Multicolor recording is easily achieved by this method using a plurality of ink nozzles. Several methods for multicolor recording using ink-jet systems have been studied. In monochrome recording, such as by a terminal printer, each point on a recording paper can be subjected to only one recording operation; therefore, satisfactory ink-jet recording is obtainable with fine paper, rolled paper for payment slips or kinds of paper having ink absorptivity slightly greater than those previously mentioned. However, in multicolor ink-jet recording, ink is squirted from two or more nozzles, and with two or more ink dots frequently merging at one point on the recording paper, more ink is used per unit area than in monochrome recording. When multicolor ink-jet recording is performed on sized paper such as fine paper or pigment-coated paper, such as art paper or coated paper insufficient wetting with ink and low ink absorptivity can cause problems, such as overflowing of ink from the point of impact, mixing of different colors of ink to give an undesired color, flying of ink to cause background smearing of the paper, and defacing of the paper upon rubbing of the recorded image. For these reasons, papers of low ink absorptivity such as fine paper, art paper and other coated papers have been unsuitable for commercial multicolor ink-jet recording.

To overcome the above-mentioned problems, for multicolor ink-jet recording, a recording paper of high ink absorptivity may be used. Paper such as filter paper made low in density without using a sizing agent wets well with ink and has interstices in the layer of paper to provide a degree of ink absorptivity sufficient to achieve multicolor ink-jet printing. There are problems with this paper also, however. An ink dot spreads on such paper and, at the same time, penetrates deep into the paper. The excessive spreading of ink dots gives low resolution, and deep penetration of the ink makes the recorded image whitish, due to light scattering caused by the interstices in the upper layer of the paper. If four-color (cyan, magenta, yellow and Indian ink) recording is effected on paper of such high ink absorptivity, the depth of penetration of the first ink drop in the paper is sufficient to reduce its visibility from above, resulting in poor color reproduction. Thus, when paper of high ink absorptivity is used in multicolor ink-jet recording, there is no overflowing, mixing or flying of ink, but the image obtained has low density, low resolution and poor color reproduction. These defects are particularly conspicuous when half-tone reproduction is desired in the multicolor ink-jet recording.

The techniques described in Japanese Patent Application (OPI) Nos. 73012/77 (the term "OPI" as used herein refers to a "published unexamined Japanese patent application"), 74340/77 and 49113/78 are intended to minimize the spreading and penetration of ink into the recording paper while holding the reduction in ink absorptivity to a minimum. However, retention of ink absorptivity is basicaly incompatible with reduced ink spreading and penetration, and an ink absorptivity in a range sufficient to permit multicolor ink-jet recording is unavoidably accompanied by undesirable spreading and penetration of the ink. In other words, since the ink-jet recording papers contemplated by these disclosures presuppose the absorption of ink into the paper, they are not capable of providing a sharp image of high density, high resolution and good color reproduction; in particular, such papers are unsuitable for use in multicolor ink-jet recording wherein half-tone reproduction is required. To summarize, to produce an image of high density, high resolution and good color reproduction by multicolor ink-jet recording, recording paper satisfying the following apparently incompatible requirements is needed: (a) ink should not spread excessively on the paper; (b) as much ink as possible should remain on the surface of paper without penetration; and (c) there should be no overflowing, mixing or flying of the ink.

It is one object of this invention to provide an ink-jet recording sheet free from overflowing, mixing and flying of ink and which provides an image of high density and resolution.

It is another object of this invention to provide an ink-jet recording sheet suitable for multicolor ink-jet recording and which is free from overflowing, mixing and flying of ink and provides an image of high density and resolution. It is a particular object of this invention to provide an ink-jet recording sheet suitable for multicolor ink-jet recording requiring faithful half-tone reproduction.

The present inventors have found that by applying a coating of water-soluble polymer to a support of low water absorptivity, an ink-jet recording sheet is obtained having a uniform layer of the coating of water-soluble polymer which does not penetrate into the support. Despite the fact that the resulting sheet does not have the degree of ink absorptivity heretofore considered necessary for ink-jet recording, it has been found that the recording sheet is capable of providing an ink-jet recorded image of good quality without causing undesired overflowing, mixing and flying of ink.

More specifically, according to this invention, an ink-jet recording sheet is provided which comprises a layer of water-soluble polymer coating disposed on a support having a water absorptivity (JIS P8140) of not more than 30 g/m^2. This JIS P8140-1976 defines a testing method for water adsorptiveness of paper and paperboard (Cobb Test).

preferred supports have a water absorptivity of not more than 20 g/m^2. This standard (JIS P8140-1976) defines a method of testing a water absorptiveness when one-sided surface of each of paper and paperboard having no absorbing property is contacted with water for a certain period of time. The contact time is usually about 120 seconds. However, the contact times vary in the range of about 60 seconds to 300 seconds in accordance with a purpose of the test and a kind of the paper used. Further, the water absorptivity is determined by the following equation:

$A = 100W$ A: Water absorptivity (g/m^2)
W: An increase of the mass of the test piece used (g)

If a porous material such as paper or cloth is used as the support, it is necessary to reduce the water absorptivity of the support by treating it with a water-repellant.

Paper used as the support in this invention is primarily made of wood pulp which may be mixed with synthetic fiber, synthetic pulp or inorganic fiber. The paper may have incorporated therein a sizing agent, such as rosin, alkyl ketene dimer or alkenyl succinic acid; a filler, such as clay, talc or calcium carbonate; a paper strength modifier, such as polyacrylamide or starch; a fixing agent, such as aluminum sulfate or cationic polymer; a wet strength modifier, such as melamine resin or polyamide-polyamine-epichlorohydrin resin; a dye and a fluorescent brightening agent.

If paper is used as the support, it is necessary that the paper contain or be coated with a sizing agent so that it has a water absorptivity of less than 30 g/m^2; again this is necessary for providing the surface of the support with a uniform coating of water-soluble polymer which does not penetrate the support. If a coating of water-soluble polymer is applied to a support comprising an unsized or low-size paper having a water absorptivity of more than 30 g/m^2 as described in Japanese Patent Application (OPI) Nos. 53012/77, 74340/77 and 49113/78, the water-soluble polymer will penetrate the paper without forming a layer on the surface of the paper. A web of paper may be passed through a size press to be coated with a water-soluble polymer such as starch or polyvinyl alcohol or a sizing agent such as sodium salt of alkyl ester of styrene-maleic anhydride copolymer.

If desired, a coating of pigment of low water absorptivity and high opacity and whiteness may be disposed beneath the layer of water-soluble polymer as a subbing layer. By virtue of the subbing layer, an ink-jet recorded image of higher density and better contrast can be obtained. Specific examples of the pigments used as a subbing layer include titanium white, kaolin and calcium carbonate. In this case, the ammonium salt of half-isopropyl ester of styrene and maleic anhydride copolymer, ammonium salt of butyl acrylate and acrylic acid copolymer, etc. can be used as a binder.

The coating of water-soluble polymer can be applied with a machine commonly employed in the coating of paper, such as an air-knife coater, blade coater, bar coater, gravure coater or curtain coater. However, machines such as a size press and roll coater which are unable to form a uniform coating on a support are not suitable for preparing the recording sheets of this invention. After a coating solution containing the water-soluble polymer has been applied and dried, it is desirable that the coating surface be rendered smooth by using a machine calender, gloss calender or supercalender.

An aqueous ink is generally employed in ink-jet recording, and the ink-jet recording sheet of this invention is used in combination with aqueous ink. The aqueous ink used in ink-jet recording on the sheet of this invention may contain a water-soluble dye, wetting agent, dye solubilizer, mildew-proofing agent, water or water-miscible organic solvent as taught in, for example, Japanese Patent Application (OPI) Nos. 12105/72, 89534/74, 97620/74, 143602/75, 102407/75, 129310/76, 137506/76, 137505/76, 115106/76, 139408/76, 12008/77, 12009/77, 12010/77, 74406/77, 77706/78, 119107/78 and 119108/78, and Japanese Patent Publication Nos. 14643/77, 14644/77 and 20882/78.

The ink-jet recording sheet according to this invention has the following advantages: (a) there is no overflow, mixing or flying of ink; (b) there is high image density; (c) minimum spreading of ink dots gives high resolution; and (d) good color reproduction is achieved in multicolor ink-jet recording.

This invention is hereafter described in greater detail by reference to the following Examples and Comparative Examples, which are illustrative, and not limiting.

Example 1

100 parts of LBKP were beat to a freeness (C.S.F.) of 430 cc and mixed with 5 parts of talc, 1 part of rosin and 2 parts of aluminum sulfate. The mixture was run on a Fourdrinier machine to provide a web of raw paper having a basis weight of 100 g/m^2. A size press was used to coat the web with a sodium salt of isopropyl ester of styrene-maleic anhydride copolymer in a dry weight of 1 g/m^2. The raw paper had a water absorptivity of 19.5 g/m^2 as measured in accordance with JIS P8140. A coating solution (solids content of 25%) consisting of 100 parts of gelatin and 200 parts of talc was applied to one side of the raw paper with an air-knife coater in a dry weight of 10 g/m^2. After drying, the raw paper was supercalendered.

Example 2

A 5% aqueous solution of polyvinyl pyrrolidone (a viscosity of 50 cps at 20°C) was applied to one surface of the raw paper of Example 1 with an air-knife coater in a dry weight of 2 g/m^2. After drying, the raw paper was

machine-calendered.

Example 3

A coating solution (solids content of 20%) consisting of 100 parts of a sodium salt of alkyl ester of styrene-maleic anhydride copolymer and 100 parts of titanium white was applied to one side of the raw paper of Example 1 with a blade coater in a dry weight of 2 g/m^2. After drying, the coated paper (or support) had a water absorptivity of 15 g/m^2 as measured in accordance with JIS P8140. A 2.5% aqueous solution of polyethylene oxide (a viscosity of 260 cps at 20°C) was applied to one surface of the support with an air-knife coater in a dry weight of 1 g/m^2. After drying, the resulting sheet was supercalendered.

Example 4

An aqueous solution containing 5% of hydroxyethyl cellulose and 0.5% of polyethyleneimine (a viscosity of 120 cps at 20°C) was applied to one surface of the raw paper of Example 1 with an air-knife coater in a dry weight of 3 g/m^2. After drying, the raw paper was machine-calendered.

Example 5

A 5% aqueous solution of sodium polystyrene sulfonate (a viscosity of 170 cps at 20°C) was applied to one surface of the raw paper of Example 1 with an air-knife coater in a dry thickness of 2 g/m^2. After drying, the raw paper was machine-calendered.

Comparative Example 1

100 parts of LBKP were beat to a freeness (C.S.F.) of 430 cc and mixed with 0.2 part of polyamide-polyamine-epichlorohydrin resin. The mixture was run on a Fourdrinier machine to provide a web of raw paper having a basis weight of 100 g/m^2.

Comparative Example 2

A size press was used to coat both sides of the raw paper of Comparative Example 1 with a 10% aqueous solution of polyvinyl pyrrolidone in a dry weight of 4 g/m^2.

Comparative Example 3

100 parts of LBKP were beat to a freeness (C.S.F.) of 430 cc and mixed with 1 part of rosin and 2 parts of aluminum sulfate. The mixture was run on a Fourdrinier machine to provide a web of raw paper having a basis weight of 100 g/m^2.

Testing

Multicolor ink-jet recording was performed on each of the recording sheets of Examples 1 to 5 and Comparative Examples 1 to 3 with four kinds of aqueous ink (cyan ink, magenta ink, yellow ink and Indian ink) squirted sequentially from four ink-jet nozzles (dia. 50 μ) of an ink-jet printer. The results are shown in Table 1 below. The recording sheets of Examples 1 to 5 according to this invention provided an image of high density without causing ink overflow. But the sheets of the Comparative Examples, prepared according to the conventional technique, experienced ink overflow, and failed to produce a high density image.

TABLE 1

	Ink*1 Overflow	Density*2	Diameter*3 of Ink Dot (μ)	Image Quality
Example 1	very good	1.45	150	very good
Example 2	very good	1.37	170	very good
Example 3	very good	1.41	170	very good
Example 4	very good	1.46	140	very good
Example 5	very good	1.40	170	very good
Comparative Example 1	very good	0.88	220-260	poor
Example 2	very good	0.95	220	good
Example 3	poor	1.13	120	poor

*1: Overflow of ink from point of mixing four colors. "Very good" means no overflow. "Poor" means no image formation due to ink overflow.
*2: Density in solid area of cyan ink.
*3: Diameter of one dot of cyan ink.

Example 6

To one surface of a corona-treated polyester film (100 μ thick), a coating solution (solids content of 20%) consisting of 75 parts of gelatin, 25 parts of polyvinyl pyrrolidone and 100 parts of silica sol was applied with

an air-knife coater in a dry weight of 5 g/m^2. Multicolor ink-jet recording was performed on the resulting film in the same manner as in the testing of the previous Examples. No ink overflow occurred, and the film provided a sharp image of high density when observed by either reflected light or transmitted light.

CLAIMS

1. A recording sheet for ink-jet recording comprising a layer of water-soluble polymer coating on a support having a water absorptivity of not more than 30 g/m^2 when measured by contacting with water for a specific time in accordance with JIS P8140 as herein described.
2. A recording sheet as claimed in Claim 1, wherein the specific time in the testing method of JIS P8140 is 120 seconds.
3. A recording sheet as claimed in Claim 1 or 2, wherein the water absorptivity of said support is not more than 20 g/m^2.
4. A recording sheet as claimed in any preceding Claim, wherein said support is selected from paper, cloth, plastics film, metal sheet, wood board and glass sheet.
5. A recording sheet as claimed in Claim 1, 2 or 3, wherein said water-soluble polymer has a viscosity of from 5 to 5,000 cps, as a 5% aqueous solution.
6. A recording sheet as claimed in Claim 5, wherein said water-soluble polymer has a viscosity of from 10 to 100 cps, as a 5% aqueous solution.
7. A recording sheet as claimed in any preceding Claim, wherein said water-soluble polymer coating is present in a dry weight amount of from 0.5 to 10 g per square meter of the support.
8. A recording sheet as claimed in Claim 7, wherein said water-soluble polymer coating is present in a dry weight amount of from 2 to 5 g pe square meter of the support.
9. A recording sheet as claimed in any preceding Claim, wherein said water-soluble polymer is selected from sweet potato starch, potato starch, corn starch, *konnyaku* glucomannan, extract of *funori* agar, sodium alginate, extract of *Hibiscus manihot*, gum tragacanth, gum arabic, locust bean gum, guar gum, pectin, carrageenan, glue, gelatin, casein, soybean protein, oxidized starch, dextrin, starch phosphate, carboxymethylated starch, hydroxyethylated starch, cyanoethylated starch, acrylic acid grafted starch, cationic starch, methyl cellulose, hydroxyethyl cellulose, carboxymethyl cellulose, cellulose sulfate, cyanoethyl cellulose, polyvinyl alcohol, carboxylated polyvinyl alcohol, polyvinyl methyl ether, sodium polyacrylate, the partially saponified product of polyacrylate ester, methyl-vinyl ethemaleic anhydride copolumer, ethylene-maleic anhydride copolymer, styrene-maleic anhydride copolymer, vinyl acetate-maleic anhydride copolymer, sodium polystyrene sulfonate, sodium polyvinyl sulfonate, sodium poly-2-acrylamide-2-methylpropane sulfonate, polyvinylbenzyl trimethylammonium chloride, polydiallyl dimethylammonium chloride, hydrochloride of polydimethylaminoethyl methacrylate, polymethacryloyloxyethyldimethyl-β-hydroxyethylammonium chloride, polyvinyl pyridine, polyvinyl imidazole, polyethyleneimine, polyamide-polyamine, lonene type quaternary ammonium salt polymer, polyacrylamide, polyethylene oxide and polyvinyl pyrrolidone.
10. A recording sheet as claimed in Claim 9, wherein said water-soluble polymer is gelatin.
11. A recording sheet as claimed in Claim 9, wherein said water-soluble polymer is polyvinyl pyrrolidone.
12. A recording sheet as claimed in any preceding Claim, wherein said layer of water-soluble polymer coating also contains a pigment.
13. A recording sheet as claimed in Claim 12, wherein said pigment is selected from clay, talc, calcium carbonate, barium sulfate, zinc oxide, titanium white, synthetic silicate, silia, diatomaceous earth, finely powdered polyethylene, finely powdered polystyrene and finely powdered urea resin.
14. A recording sheet as claimed in Claim 12 or 13, wherein said pigment is present in an amount of up to 10 parts by weight per part of said water-soluble polymer.
15. A recording sheet as claimed in any preceding Claim and further comprising a layer of pigment of low water absorptivity between said support and said layer of water-soluble polymer coating.
16. A recording sheet as claimed in Claim 1 and substantially as herein described.
17. A recording sheet substantially as herein described with reference to any one of Examples 1 to 6.
18. The features as herein disclosed, or their equivalents, in any novel selection.

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